CCL REPORT NO. 307

FINAL REPORT

DEVELOPMENT OF A PHOSPHATE-FREE ALKALINE CLEANER PAINT STRIPPER

BY

TROY R. NICHOLS

JULY 1972

U. S. ARMY
ABERDEEN RESEARCH & DEVELOPMENT CENTER
COATING & CHEMICAL LABORATORY

Aberdeen Proving Ground
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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U.S. Army Aberdeen Research & Development Center Coating & Chemical Laboratory Aberdeen Proving Ground, MD 21005	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP
3. REPORT TITLE DEVELOPMENT OF A PHOSPHATE-FREE ALKALINE CLEANER - PAINT STRIPPER	
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report	
5. AUTHOR(S) (First name, middle initial, last name) NICHOLS, Troy R.	

6. REPORT DATE July 1972	7a. TOTAL NO. OF PAGES 19	7b. NO. OF REFS 7

8a. CONTRACT OR GRANT NO. AMCMS Code No. 502E.11.80300 b. PROJECT NO. 1T062105A109 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) CCL No. 307 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited. [redacted]	
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U.S. Army Materiel Command Washington, D. C. 20315

13. ABSTRACT

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DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED
Security Classification

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT

Security Classification

UNCLASSIFIED

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DEVELOPMENT OF A PHOSPHATE-FREE ALKALINE CLEANER PAINT STRIPPER

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AMCMS CODE NO. 502E.11.29500

DEPARTMENT OF THE ARMY PROJECT NO.
1T062105A109

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A phosphate-free composition was developed for use either as an alkaline paint remover or as an alkaline cleaner. Used as a paint remover at its optimum solution concentration of 12.0%, the performance of the composition compares favorably to that of the class 1 paint remover of Federal Specification TT-R-230B; at 4.0% the performance is superior to that of the class 2 paint remover of TT-R-230B; and at 3.1% the performance is about equal to that of the alkaline cleaner of Federal Specification P-C-436C.

TABLE CONTENTS

I. INTRODUCTION

Powdered compounds dissolved in water solutions are utilized for most cleaning and paint stripping operations during manufacture, overhaul, and rebuild of material. They are perferred over solvent types because they are easy to handle, relatively nontoxic, non-flammable, and can normally be disposed of by standard waste discharges. In recent years concern has been expressed about the contents of water discharges from arsenals, depots, and manufacturers engaged in production of equipment. One of the major areas of concern has been with phosphates in such compounds because of the eutrophication of streams and waterways.

Phosphates have been labeled as one of the important contributors to the eutrophication of streams and waterways (1 and 2), and because of this wide-spread efforts are being made to replace or reduce them in all types of cleaners (3 and 4). Some localities have passed laws requiring their reduction in or total elimination from household cleaning compounds (5, 6, and 7).

Phosphates are commonly used in alkaline cleaners and in alkaline paint strippers to increase efficiency. The method by which phosphates perform is complex and not entirely understood. However, they are known to deflocculate certain soils and to sequester unwanted metal ions under certain conditions. In addition, phosphates provide a reserve alkalinity and, therefore, help maintain a constant pH value during the cleaning or paint-stripping operation.

This report describes the development of a phosphate-free composition which can be used either as a cleaner or as a paint stripper depending on concentration. The composition is suitable for replacing the alkaline cleaner of Specification P-C-436C (Table I) and both of the paint removers of Specification TT-R-230B (Tables II and III).

II. DETAILS OF TEST

The test methods used in this investigation were the performance tests of Federal Specifications TT-R-230B and P-C-436C. The concentration of the test solution of the developed phosphate-free composition was adjusted to give the greatest effectiveness for the specific use. That is, the solution concentration of the phosphate-free composition was:

12.0% when tested according to Spec TT-R-230B for class 1,
4.0% when tested according to Spec TT-R-230B for class 2,
3.1% when tested according to Spec P-C-436C.

The alkaline paint remover specification TT-R-230B lists two classes of strippers; class 1 for use with ferrous and magnesium metals; class 2 for use with non-ferrous and aluminum metals. The formulas for these two products and for the alkaline cleaner P-C-436C are shown in Tables I, II, and III. Data for establishing concentration, surfactant ratios and

amounts of corrosion inhibitor are presented in Tables IV, V and VI. Table VII shows comparative penetration data, for establishing optimum free-flowing characteristics. Tables VIII, IX and X compare the performance of proposed new phosphate-free cleaners to that of the original specification materials (P-C-436C and classes 1 and 2 of TT-R-230B). Cost comparisons are shown in Table XI.

III. RESULTS AND DISCUSSION

Several corrosion inhibitors were screened for protection of aluminum in a phosphate-free alkaline cleaner solution based on sodium metasilicate and an anionic detergent. Potassium chromate was found to protect aluminum from corrosion up to a pH value of 12.8. However, the concentration of potassium chromate required was about 7.5% of the total cleaner composition, and this would have introduced disposal problems. Two other inhibitors, 2-mercaptobenzothiazole and 1,3 di-n-butyl-2-thiourea, were tried separately at 7.5% of the total cleaner composition, but neither could protect aluminum from corrosion in an alkaline cleaner solution having a pH of 12.8. The most effective corrosion inhibitors tested were sodium stannate and potassium stannate. The stannates were selected as the basic inhibitor systems for all studies relative to optimizing the replacement formulations.

The standard comparison compound of Spec P-C-436C (Table I) is used at a solution concentration of 4.75%, pH value 12.2, and is non-corrosive to aluminum. This composition modified by using a 98% active anionic for the 40%, omitting the phosphates, and making the remainder sodium metasilicate can be made non-corrosive to aluminum by addition of sodium or potassium stannate (Table IV). Only the solution concentration of sodium stannate (or potassium stannate) is varied in the tests of Table IV and the pH value is 13.0 in each test. The lower limit for protection of aluminum 1100 against corrosion, when tested as specified in Spec P-C-436C paragraph 4.4.2, is about 1.2% for either sodium or potassium stannate (compositions 3 and 7).

The lower limit of the solution concentration of compostion 7 (Table IV) for satisfactory cleaning when tested according to Spec P-C-436C is about 2.0 percent, corresponding to a pH value of 12.8 (Table V). At this concentration the composition passes the mineral oil cleaning test and cleans the asphalt soiled panels as readily as does the standard comparison compound.

The most effective ratio of nonionic surfactant to anionic surfactant for asphalt cleaning at a pH of 12.8 is about 0 5 (Table VI), which is the ratio used in composition 7 (Table IV). The solution concentration of only the nonionic is varied in these tests.

Composition 7 (Table IV) has a lower penetration value than does the comparison compound of Spec P-C-436C. Penetration test data is shown in Table VII. This indicates a less granular quality, and past experience would indicate it might lump or cake badly on storage. Actually the composition does become less free-flowing during storage.

The penetration value of the phosphate-free composition can be raised to an acceptable level, however, by using the pentahydrate instead of the anhydrous form of sodium metasilicate (composition 9, Table VII). The mole ratios of the ingredients in composition 9 are the same as in composition 7. Composition 9 must be used at a higher concentration than composition 7. The use concentrations for alkaline cleaning at a pH of 12.8 are indicated in column 2. At these solution concentrations the molar concentration of each ingredient does not change from one cleaner to another. Compositions 10 and 11 (Table VII) are modifications of compositions 7 and 9 respectively: a 40% active dodecylbenzene sodium sulfonate is substituted for the 98% active, with all mole ratios kept constant. Of these 4 compositions only number 9 has a penetration value as high as the standard comparison compound of Spec P-C-436C (Table VII).

Composition 9 (Table VII), the phosphate-free composition with the highest penetration value, at a solution concentration of 3.10% as a cleaner passes all the performance requirements of Spec P-C-436C except the pH value (Table VIII). Although the pH value of composition 9 exceeds that of the comparison compound of Spec P-C-436C, the aluminum corrosion is no greater than that of the comparison compound.

At a solution concentration of 4.0%, composition 9, as a stripper, passes all the performance tests for the class 2 paint remover of Spec TT-R-230B except that for the pH value (Table IX). This paint remover is normally used at 9.0% for stripping paint from aluminum. The higher pH value of composition 9 at 4.0% is not considered a disadvantage as this solution does not corrode aluminum.

At a solution concentration of 12.0%, composition 9 compares favorably with the class 1 paint remover of Spec TT-R-230B. This paint remover is normally used at 9.0% for removing paint from ferrous and magnesium metals. The 12.0% solution of composition 9 has a lower pH value than the test solution of the standard comparison compound and is slower in removing paint (Table X). The paint removal time may exceed that of the comparison compound by as much as 200%, but this may not prove a disadvantage as the maximum time for stripping is no more than two minutes.

Based on cost of ingredients, composition 9 could be used to replace the alkaline cleaner of Spec P-C-436C with a savings of 45% and the class 2 paint remover of Spec TT-R-230B with a savings of 38% (Table XI). Replacing the class 1 paint remover of Spec TT-R-230B with composition 9 would result in an increase in cost of 55%.

IV. RECOMMENDATION

In view of its successful performance, a large scale caking-in-storage test of the phosphate-free composition is planned. Also, it is intended to have the phosphate-free composition field-tested as an alkaline cleaner and as an alkaline paint remover. Satisfactory field tests and caking-in-storage test could be followed by a proposed specification replacing both Specifications P-C-436C and TT-R-230B.

V. REFERENCES

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APPENDIX A

TABLE I

Standard Comparison Compound of
Federal Specification P-C-436C

	Percent by Weight
Sodium metasilicate, anhydrous	31.3
Primary sodium phosphate, monobasic, anhydrous	12.3
Trisodium phosphate, anhydrous	24.8
Nonionic surfactant, poly (9-10) oxyethylene octyl phenol	7.9
Anionic surfactant, straight chain sodium alkyl benzene sulfonate, 40 percent active	23.7

TABLE II

Composition of Specification TT-R-230B
Class 1 Comparison Compound

	Percent by Weight
Sodium hydroxide	63.0
Trisodium phosphate anhydrous	35.0
Dodecyl benzene sodium sulfonate, 86% active	2.0

TABLE III

Composition of Specification TT-R-230B
Class 2 Comparison Compound

	Percent by Weight
Sodium metasilicate pentahydrate	35.0
Trisodium phosphate dodecahydrate	47.8
Dodecyl benzene sodium sulfonate, 86% active	5.0
Potassium chromate	0.2
Sodium phosphate monobasic, monohydrate	12.0

TABLE IV

Determination of Lower Limit of Corrosion Inhibitor for Protection Aluminum 1100 at a pH of 13.0

Composition	% Solution g/100 ml.	% by Weight: Na_2SiO_3 Anhydrous	% by Weight: Nonionic Surfactant*	% by Weight: Anionic Surfactant**	% by Weight: Potassium Stannate	% by Weight: Sodium Stannate	Aluminum 1100 Corrosion, mg Weight Change
1	2.62	76.30	7.90	15.80	--	--	1.3, 1.4, 1.3, 1.3 loss
2	2.83	70.67	7.42	14.84	--	7.07	0.2, 0.2, 0.2, 0.2 gain
3	2.66	75.10	7.89	15.77	--	1.24	0.0, 0.1, 0.1, 0.2 gain
4	2.66	75.19	7.89	15.79	--	1.13	0.0, 0.1, 0.1, 0.1 loss
5	2.91	68.73	7.22	14.43	9.62	--	0.0, 0.2, 0.2, 0.2 gain
6	2.67	74.93	7.87	15.74	1.46	--	0.0, 0.1, 0.1, 0.1 gain
7	2.66	75.10	7 89	15.77	1.24	--	0.0, 0.0, 0.0, 0.0
8	2.66	75.19	7.89	15.79	1.13	--	0.0, 0.0, 0.1, 0.1 loss

*Poly (9-10) oxyethylene octyl phenol.
**Linear dodecylbenzene sodium sulfonate, 98%.

TABLE V

Determination of Minimum Solution Concentration of Composition 7 Necessary for Satisfactory Cleaning

	% Solution, g/100 ml.	pH Value	Mineral Oil Cleaning	Asphalt Cleaning, minutes for removal
	2.00	12.8	Passes	10, 12, 11
	1.33	12.7	Passes	19, 17, 19
Spec P-C-436C Standard Comparison Compound	4.75	12.2	Passes	10, 12, 12

TABLE VI

Determination of Most Effective Ratio of Surfactants in Solution Maintained at a pH of 12.8

Ratio		% by Weight				
Nonionic Surfactant / Anionic Surfactant	% Solution, g/100 ml.	Na_2SiO_3 Anhydrous	Nonionic Surfactant*	Anionic Surfactant**	Potassium Stannate	Asphalt Cleaning, minutes for removal
0.64	2.05	73.5	9.9	15.4	1.2	12, 12, 11
0.50	2.00	75.1	7.9	15.8	1.2	10, 12, 11
0.45	1.99	75.7	7.1	15.9	1.3	12, 13, 13
0.38	1.97	76.5	6.1	16.1	1.3	14, 13, 15

*Poly (9-10) oxyethylene octyl phenol.
**Linear dodecylbenzene sodium sulfonate, 98%.

TABLE VII

Effect of Hydrated Sodium Metasilicate on Penetration

		% by Weight						
	Use				Surfactant, active **			
Composition	Concentration, g/100 ml.	Na_2SiO_3 Anhydrous	Na_2SiO_3 $5 H_2O$	Nonionic Surfactant*	98%	40%	Potassium Stannate	Penetration Values
7	2.00	75.1	--	7.9	15.8	--	1.2	92-113
9	3.10	--	84.0	5.1	10.1	--	0.8	191-198
10	2.48	60.8	--	6.4	--	31.8	1.0	145-166
11	3.57	--	72.9	4.4	--	22.0	0.7	153-166
Spec P-C-436C Standard Comparison Compound								178-184

*Poly (9-10) oxyethylene octyl phenol.
**Linear dodecylbenzene sodium sulfonate.

TABLE VIII

Performance Tests of Spec P-C-436C

	Standard Comparison Compound, 4.75% solution	Composition 9, 3.10% solution
Cleaning Efficiency		
Mineral Oil		
Asphalt	Passes 10-12 minutes for removal	Passes 10-12 minutes removal
Stability Test		
Mineral Oil		
Asphalt	Passes 11-13 minutes for removal	Passes 10-13 minutes for removal
Corrosion,		
Aluminum 2024	0.1, 0.1, 0.2, 0.2 mg gain	0.1, 0.1, 0.2, 0.2 mg gain
Galvanic Corrosion		
Aluminum 2024	0.5, 0.5, 0.9, 0.9 mg gain	0.1, 0.2, 0.2 0.5 mg gain
Magnesium AZ31B	1.1, 1.4, 1.8, 1.9 mg gain	1.4, 1.5, 1.5, 1.7 mg gain
pH value	12.2	12.8
Penetration	178-184	191-198
Rinsing	Passes	Passes

TABLE IX

Performance Tests, Class 2 Paint Remover of Spec TT-R-230B

	Class 2 Standard Comparison Compound, 9.0% solution	Composition 9, 4.0% solution
Paint Stripping		
Paint System		
1	3 - 3-1/4 minutes for stripping	2 - 2-1/4 minutes for stripping
2	6-3/4	4-3/4 - 5
3	10-1/2 - 11	6-3/4 - 7
4	3-3/4 - 4	2-3/4 - 3
Stability		
Paint System		
1	3-1/4 - 3-1/2	1-3/4 - 2
2	7-1/4 - 7-1/2	4-3/4 - 5
3	11-- 11-1/4	6-3/4 - 7
4	2-3/4 - 3	2-1/4 - 2-1/2
pH value	12.2	13.0
Corrosion, Aluminum 1100	0.2, 0.2, 0.2, 0.3 mg gain	0.0, 0.0, 0.0, 0.0 change
Rinsing	Passes	Passes

TABLE XI

Cost Comparison Based on Cost of Ingredients

	Specification Compound		Composition 9		Reduction, or Increase, in Cost Using Composition 9
	Cost per lb., Dry Basis	Cost per Gal., of Solution	Cost per lb., Dry Basis	Cost per Gal., of Solution	
Alkaline Cleaner of P-C-436C	$0.117	$0.051	$0.107	$0.028	45% reduction
Paint Remover of TT-R-230B					
Class 1	$0.091	$0.069	$0.107	$0.107	55% increase
Class 2	$0.078	$0.058	$0.107	$0.036	38% reduction